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STUDIES OF THE DELAYED NEUTRONS
II. CHEMICAL ISOLATION OF THE 56-SECOND AND THE 23-SECOND ACTIVITIES

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Arthur H. Snell J. S. Levinger
E. P. Meiners, Jr. M. B. Sampson
R. G. Wilkinson

University of Chicago

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ABSTRACT

The 23-second delayed neutron activity is found to follow the chemistry of iodine, and the 56-second delayed neutron activity is found to follow the chemistry of bromine. Comparison with known beta emitters of like half-lives suggests that the neutron-emitting nuclei may be Xe^{137} and Kr^{87}.

* * * * *

In the preceding paper, resolution of the decay curve of the delayed neutrons resulting from the fission of uranium is described. Activities with half-lives of 0.4, 1.8, 4.4, 23, and 56 seconds were found. The fact that discrete decay periods are present is good evidence in favor of the interpretation put forward by Bohr and Wheeler[1] of the existence of delayed neutrons, namely that they originate in the fission products, and are emitted when the beta-decay of a fragment leaves the nucleus in a state of excitation higher than the binding energy of a neutron in that nucleus. The neutron is then immediately emitted, and the rate of decay of the neutron-emitting activity observed is just that of the preceding beta-activity. In this paper we shall describe successful chemical isolation of the 56-second and the 23-second activities in the fission products.

EXPERIMENTAL PROCEDURE AND RESULTS

Most of the irradiations were made with the University of Chicago cyclotron, using 7.3 Mev deuterons on beryllium as a neutron source. Beam currents ranged up to 100 microamperes, giving in the paraffin-surrounded sample a slow neutron flux of about 10^9 neutrons per cm^2 per sec. The samples were usually a few hundred milliliters of aqueous solution of uranyl nitrate. The counting was done with a boron trifluoride proportional counter having a total boron cross section of about 2 cm^2, surrounded with several inches of paraffin. The counting was done by three workers; one called the time, the second read the scaler, and the third recorded the readings. During the early part of the decay the accumulating count was recorded every 5 seconds, but as the activity became weaker this interval was lengthened to 10 seconds and finally to 30 seconds.

The problem on first approach looked like a difficult one, namely, to identify within the time limit for chemistry of about one minute, one or two of the thirty-odd fission product elements. With the idea of at least narrowing down on the possibilities, we made a number of experiments which led to negative results. It seems, nevertheless, worth while to mention them briefly because some of them rule out possibilities for the still unidentified shorter activities, and others give evidence against the odd chance of the presence in the elements concerned of activities with about the same decay periods as those which we have been able to extract.

1) Sulphate precipitation: We irradiated 250 cc aqueous solution containing 40 g uranyl nitrate, fission product carrier, and barium nitrate. After irradiation we added sulphuric acid, filtered, and examined the precipitate. Only a very weak neutron-emitting activity was found in the precipitate 30 seconds after the stop of the activation.

2) Water extraction from ether solution: We irradiated 80 g of uranyl nitrate dissolved in 500 cc ethyl ether in a separating funnel, with 10 cc water and fission product carrier. After irradiation, the liquid was shaken, allowed to settle, and the water was drained off. Most of the neutron-emitting activity remained in the ether subsequent to 40 seconds after stop of activation.

3) Barium: A barium chloride precipitate was taken from the water layer following an ether extraction. Only very weak activity was found in the precipitate 60 seconds after stop of activation. In other experiments, aqueous solutions were activated and barium chloride precipitates were taken out after irradiation. The precipitates had no neutron-emitting activity 40 seconds after the stop of activation.

4) Rare gases: (a) A flask containing an aqueous solution of uranyl nitrate was boiled under reduced pressure while under irradiation. An air stream was led through a flask to a NaOH trap, and thence to a charcoal trap. A weak neutron-emitting activity built up in the NaOH trap, but none in the charcoal, although the latter became beta active. (b) 1400 cc of uranyl nitrate solution containing 100 grams of the nitrate were irradiated, and after irradiation allowed to pour through a pipe into another vessel in which the boron trifluoride counter was set. A decay curve was taken. Then the experiment was repeated except that the solution was kept boiling during activation. The boiling should have greatly weakened any rare gas activities, but the decay curves were of the same shape and the activities were of about the same intensity subsequent to 10 seconds after stop of activation.

Experiments which gave positive results started after we tried a silver halide precipitation, and found that both the 23-second and the 56-second activities came down very strongly. Since silver selenite and presumably tellurite also would have precipitated from the solution, we made separations from solutions which had been made strongly acid with HNO_3, under conditions such that (as we verified by trial) silver selenite would not precipitate. The 23-second and 56-second activities still came down with the silver halide. This evidence that these activities were distributed between bromine and iodine seemed not to be in disagreement with the results of experiments described in the preceding paragraph.

THE IODINE ACTIVITY

About 150 cc of an aqueous solution of uranyl nitrate were irradiated for 2 minutes in a separating funnel. A few milligrams of KI and KBr were present to act as carrier, and a few cc of carbon tetrachloride were present. The concentration of the uranyl nitrate solution was held down so that the carbon tetrachloride would settle promptly after the funnel had been shaken. One cc of concentrated HCl was present in the solution, and after irradiation, 10 cc of 5% sodium nitrite solution were added. Following shaking and settling, the carbon tetrachloride layer (colored violet by the iodine) was drawn off and counted. The result was a single exponential decay with a half-life of 24 seconds, covering the time interval 30 seconds to 200 seconds after stop of irradiation.

Later we found that the sodium nitrite could just as well be present during the activation, and that repeated extractions could be made from one batch of solution. One added new carrier and new carbon tetrachloride before each activation, and did not shake until after the activation. By standardizing the procedure so that counts were always recorded at the same time after the stop of activation, we ran through eight extractions and by averaging the resulting readings we obtained the curve reproduced in Figure 1 and labeled "Iodine". It will be noticed that the first point comes at 28 seconds after the stop of activation, and that the curve is a simple exponential over an intensity factor of about 100, and that the half-life is 23.8 ± 0.7 seconds. The limits of error for this figure are those allowed by the scatter of the points.

THE BROMINE ACTIVITY

Since the 23-second delayed neutron activity appeared to follow the chemistry of iodine, it seemed very probable that the 56-second activity would follow that of bromine. A positive experiment required a specific separation for bromine in an attempt to get the longer-lived delayed neutron emitter clear of the others. This was accomplished at the Clinton Laboratories, and the experiment was as follows:

About 1 cc of uranyl nitrate solution was irradiated for 2 minutes in the Clinton pile. The transfer in and out of the pile was accomplished with the pneumatic tube arrangement. After irradiation, the sample was allowed to stand for 16 seconds to permit decay to a moderately safe level of a strong 8-second nitrogen ^{16} activity which was induced in the lucite container of the solution. Then the uranyl nitrate was poured into a separating funnel containing 30 ml of 8N nitric acid which was saturated with potassium chlorate. Br- and I-carriers were added and Br_2 and I_2 extracted with carbon tetrachloride. The carbon tetrachloride was run into a second separating funnel which contained a potassium nitrite solution made slightly acid with nitric acid. Here the bromine was reduced to bromide, the iodine being at the same time kept oxidized. The carbon tetrachloride was drained off, and the water layer counted. As in the case of iodine, we standardized times and procedures so that five good runs could be averaged. The resulting decay curve is given in Figure 1, labeled "Bromine".

For comparison, we took readings on samples of uranium nitrate irradiated for 2 min but followed by no chemical extractions. These gave the curve labeled "unseparated". The presence in the bromine of a small amount of shorter activity as indicated by the earliest two points on the bromine curve is explicable on the basis of imperfect chemical separation in the somewhat hasty manipulations involved. The isolated bromine activity seems to have a half-life of 54 ± 1 seconds, where again the limits of error are those permitted by the scatter of the points.

To compare the decay of the separated bromine with that of an unseparated sample in which other activities have fully decayed, we activated several grams of uranyl nitrate, waiting 6 minutes before starting the count. The resulting curve is labeled "Larger Sample, Unseparated" in the figure. Between 6 and 12 minutes after stop of irradiation, the slope corresponds to a half-life of 57 ± 1 seconds. This is a little longer than that of the extracted bromine, but the difference is probably attributable to experimental effects such as the presence of a little iodine in the bromine samples.

DISCUSSION

Probably the bromine and iodine activities account for all of the 23-second and 56-second activity observed in the total delayed neutron decay curve. We are not able to set very low experimental limits on the presence in other fission products of activities having about the same decay periods, but in one set of experiments we compared the intensities of silver halide precipitates with those of their filtrates. The filtrates were 5 to 10 times weaker, and this residual activity is attributable to the imperfection of the fast filtering, and to the probable presence of some activity in the form of bromates and iodates which did not precipitate. The filtrate decay curves were rough but did not require new decay periods for their description.

It is tempting to identify these two delayed neutron activities respectively with the 30 ± 6-second iodine beta activity and the 50 ± 10-second bromine beta activity found by Strassmann and Hahn.[2] Seelmann-Eggebert and Born[3] subsequently found that a 3.8-minute xenon grows from the 30 ± 6-second iodine, and a 75-minute krypton grows from the 50 ± 10-second bromine. In other work,[4] the 75-minute krypton was identified as krypton^{87} and the 3.8-minute xenon identified as probably xenon^{137}. If the possible existence of conflicting bromine and iodine beta activities had been ruled out, it would seem that the mass assignments of the delayed neutron emitters would be settled.

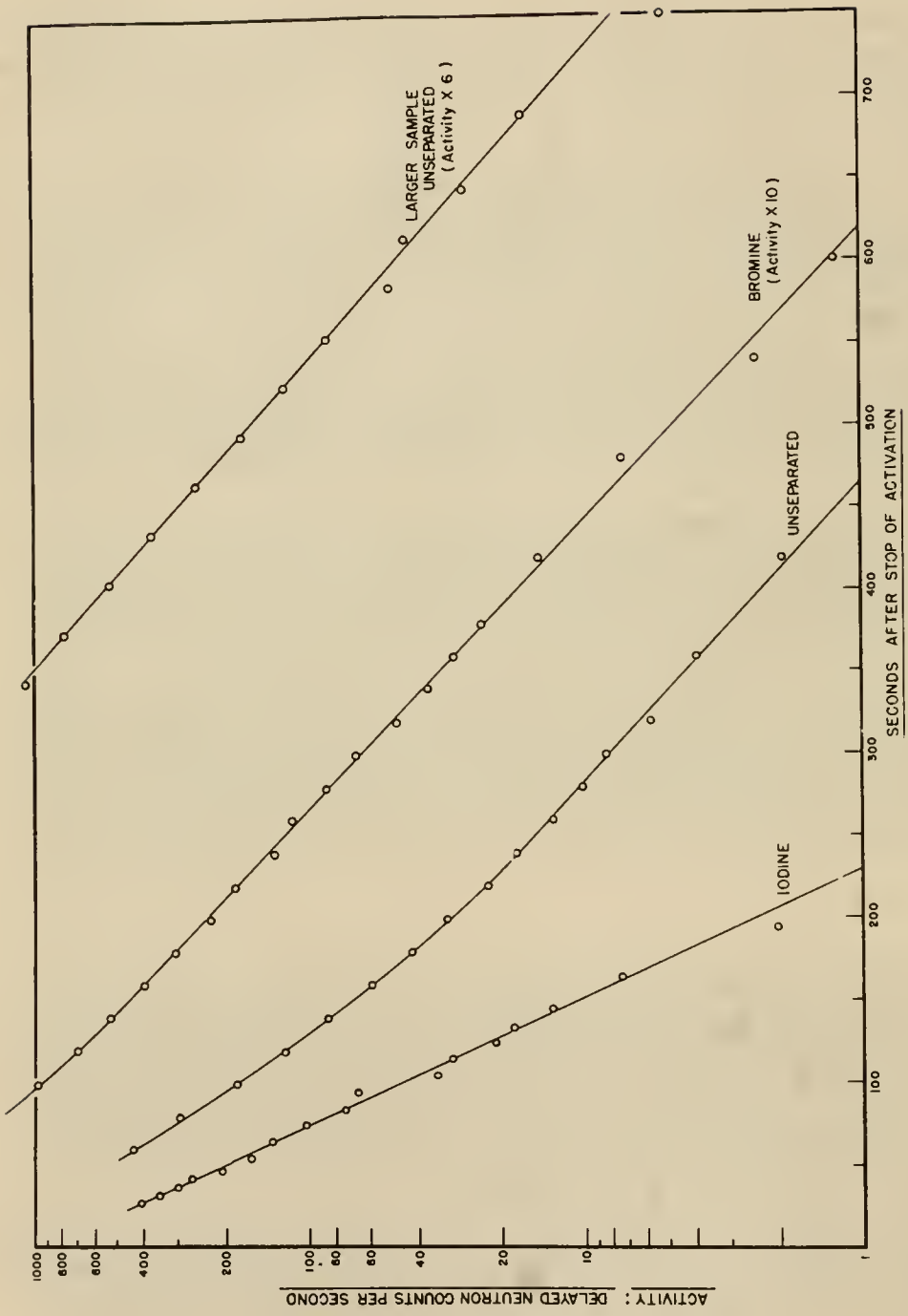

Figure 1. Decay curves of the delayed neutrons emitted from uranium ("unseparated") and from the separated iodine and bromine fission products. The decay of the longest period in the unseparated sample is seen to be parallel to that of the bromine fraction.

As it is, coincidences may exist whereby another isotope of bromine has a period close to that of bromine^{87}, or another isotope of iodine a period close to that of iodine^{137}. We did some work on the short-lived bromine and iodine beta and gamma emitters, but our results were not of direct assistance. They did indicate, however, that the 50-second bromine and the 30-second iodine are not the only short-lived halogen fission products; the situation is more complicated, both in bromine and in iodine.

A comparison of the fission product yield data with the intensity of the bromine and iodine delayed neutrons gives some information about their emission. The yields of the short-lived 87 and 137 chains have not been measured explicitly, but according to the fission product yields as determined chemically,[5] 2.5% of the fissions should lead to products of mass 87, and 6.2% should lead to products of mass 137.

On the other hand, the intensity of the delayed neutrons relative to the instantaneous neutrons* tells us that only about 0.2% of the fissions produce the 56-second delayed neutron activity, and only about 1% of the fissions produce the 23-second delayed neutron activity. Increasing the assigned masses does not bring closer agreement, and one must conclude that one or both of the following factors must be coming in: (1) a sharp drop in yield for the early members of the chain; (2) a branching decay process. Such a branching might be as indicated in Figure 2, where the mass numbers 87 and 137 are provisionally written in. Here it is assumed that the decay of the bromine (iodine) leaves a few of the krypton (xenon) nuclei in one or more states which are excited highly enough to permit neutron evaporation, but that most of the decay passes through a lower state and eventually to strontium (barium) in the conventional manner.

Bohr and Wheeler give general theoretical arguments indicating how the energy of beta transitions in some fission fragments can exceed the neutron binding energy in the product nucleus and thus lead to delayed neutron emission. The identification of the neutron-emitting nuclei as isotopes of krypton and xenon now permits closer comparison with their theory, and one can see what the Bohr-Wheeler considerations predict with regard to the mass assignments of the activities. In Table 1, we give the energies available for beta transformation and the neutron binding energies as calculated according to the method of Bohr and Wheeler for isotopes in the region with which we are concerned. It will be noticed that according to these figures delayed neutron emission would be energetically possible for bromine-krypton transitions of mass 88 or higher, and for the iodine-xenon transitions it would be possible for mass 140 or higher. Although the statistical theory probably cannot be forced to detail for individual isotopes, the figures illustrate the a priori probability that the delayed neutrons should come from nuclei heavier than 87 and 137.

Table 1. Bohr-Wheeler beta decay energies and neutron binding energies.

A	Beta transition energy in bromine Mev	Neutron binding energy in krypton Mev	A	Beta transition energy in iodine Mev	Neutron binding energy in xenon Mev
87	5.3	5.7	137	3.5	5.5
88	8.8	7.9	138	6.0	6.3
89	6.9	4.7	139	4.8	5.0
90	10.5	6.5	140	7.2	5.8
			141	6.0	4.6
			142	8.3	5.0

* Snell, A. H., et al., preceding paper.

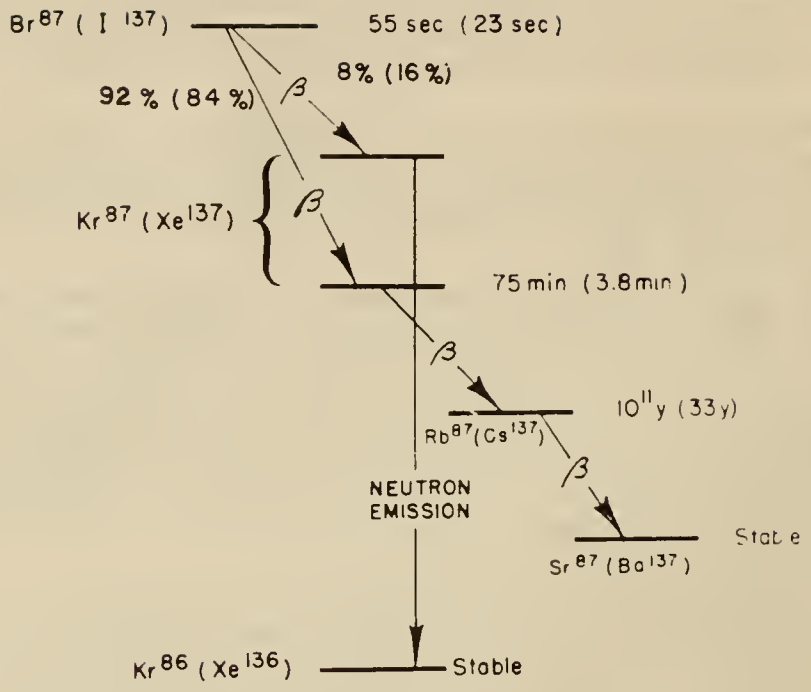

Figure 2. Possible branching mechanism which would account for the low yield of the iodine and bromine delayed neutrons in comparison with the yields of fission products of mass 137 and 87. The branching ratios have been adjusted on the assumption of the indicated mass assignments (which are uncertain), and on the basis of an initial intensity of all of the delayed neutrons equal to 1% of the intensity of the instantaneous fission neutrons.

Measurements have also been made in this laboratory upon the delayed neutrons from the fission of thorium.[6] For the most part, the same decay periods were found, but the 56-second activity was about three times more intense relative to the 23-second activity than was the case for fission of uranium 235. This can be qualitatively understood from the fission yield curve[5] if the mass numbers 87 and 137 are approximately correct. A shift of the lower mass peak toward still lower masses would increase appreciably the relative yield at mass 87, while mass 137, being near the flattened top of the other peak, would be almost unaffected. Disregarding the possibilities of changes in yield along the chain and of changes in the branching ratio for the delayed neutron emission, the thorium results may be said to imply that the bromine activity should be ascribed to a mass number less than 90. The results of Jentschke[7] for uranium 238 and thorium fission seem to indicate that the lower mass peak is more sensitive than the higher mass peak with regard to changes in the mass of the fissioning nucleus.

ATTEMPTS AT RECOIL COLLECTION

An experiment which looks attractive from the point of view of obtaining unambiguous mass assignments and also of identifying the shorter-lived emitters is that of examining the radioactivity of the nuclei which recoil because of the emission of the delayed neutrons. These recoil nuclei might be expected according to present knowledge to have an energy of a few kilovolts. We attacked the problem as follows:

Fission fragments emitted from the inner surface of a uranium cylinder about 3 inches in diameter were collected electrostatically upon the surface of a metal rod arranged axially in the cylinder. After irradiation, a paper or aluminum sleeve was slipped over (but not touching) the rod, and the cylinder was evacuated to a few millimeters pressure. The sleeve was supposed to pick up the delayed neutron recoils. Times of irradiation and times of waiting before placing the sleeve could be arranged so as preferentially to emphasize collection from any desired delayed neutron activity, and repeated collections could be made on one sleeve to build up intensity. We found that the sleeves always showed radioactivity — even when collection was started after the delayed neutrons had all decayed. This meant that activity was evaporating from the surface of the rod and blanketing the rather small effect which we sought. Variants of the experiment which we tried in attempts to reduce this effect included the application of retarding electrostatic fields, variation in pressure during the recoil collection, and cooling the rod bearing the fission fragments. Our results have been inconclusive, but the experiments might be worth pursuing under quite carefully controled conditions. Incidental considerations in the case of the bromine and iodine activities are: (1) the recoiling rare gas atom might not stay on the sleeve; and (2) if the mass assignments of 87 and 137 are correct, the recoiling nuclei are probably stable.

We are indebted to Dr. N. Sugarman for early advice on the chemical separations, and to Dr. Katherine Way for consultations on the application of the Bohr-Wheeler theory.

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